Designation: D4327 – 11

Standard Test Method for Anions in Water by Suppressed Ion Chromatography[1]

This standard is issued under the fixed designation D4327; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method[2] covers the sequential determination of fluoride, chloride, nitrite, *ortho*-phosphate, bromide, nitrate, and sulfate ions in water by suppressed ion chromatography.

NOTE 1—Order of elution is dependent upon the column used; see Fig. 1.

1.2 This test method is applicable to drinking and wastewaters. The ranges tested for this test method for each anion were as follows (measured in mg/L):

Fluoride	0.26 to 8.49
Chloride	0.78 to 26.0
Nitrite-N	0.36 to 12.0
Bromide	0.63 to 21.0
Nitrate-N	0.42 to 14.0
o-Phosphate	0.69 to 23.1
Sulfate	2.85 to 95.0

1.3 It is the user's responsibility to ensure the validity of this test method for other matrices.

1.4 Concentrations as low as 0.01 mg/L were determined depending upon the anions to be quantified, in single laboratory work. Utilizing a 50-µL sample volume loop and a sensitivity of 3 µS/cm full scale, the approximate detection limits shown in Table 1 can be achieved. Lower detection limits have been observed with newer instrumentation, column technology and eluents. The analyst must assure optimum instrument performance to maintain a stable baseline at more sensitive conductivity full-scale settings.

1.5 The upper limit of this test method is dependent upon total anion concentration and may be determined experimentally as described in Annex A1. These limits may be extended by appropriate dilution or by use of a smaller injection volume.

1.6 Using alternate separator column and eluents may permit additional anions such as acetate, formate or citrate to be determined. This is not the subject of this test method.

1.7 This method update approves the use of Electrolytically generated eluent, electrolytically regenerated eluent, electrolytic suppression (not autozeroing) and electrolytic trap columns also known as Reagent Free Ion Chromatography. This approval is based on acceptance by the US EPA as referenced in Appendix X2

1.8 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.9 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] The following references may be consulted for additional information:

Small, H., Stevens, T. S., and Bauman, W. C., "Novel Ion Exchange Chromatographic Method Using Conductrimetric Detection," *Analytical Chemistry*, Vol 47, 1975, p. 1801.

Stevens, T. S., Turkelson, V. T., and Alve, W. R., "Determination of Anions in Boiler Blow Down Water with Ion Chromatography," *Analytical Chemistry*, Vol 49, 1977, p. 1176.

Sawicki, E., Mulik, J. D., and Witgenstein, E., Editors, *Ion Chromatographic Analysis of Environmental Pollutants*, Ann Arbor Science Publishers, Ann Arbor, MI, 1978.

Mulik, J. D., and Sawicki, E., Editors, *Ion Chromatographic Analysis of Environmental Pollutants*, Vol/No. 2, Ann Arbor Science Publishers, Ann Arbor, MI, 1979.

Weiss, J., *Handbook of Ion Chromatography*, Dionex Corp., Sunnyvale, CA, 1986.

Waters Innovative Methods for Anion Analysis, Waters Chromatography Division of Millipore, Method A 107 and A 116, 1990.

Haddad, P. R., and Jackson, P. E., *Ion Chromatography: Principles and Applications*, Elsevier Scientific Publishing Co., 1990.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

***A Summary of Changes section appears at the end of this standard**

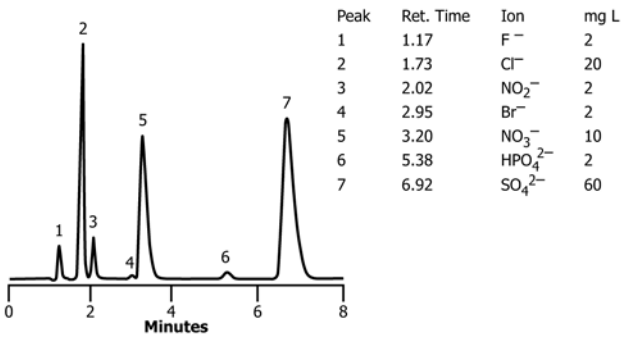

FIG. 1 Chromatogram Showing Separation Using the AS4A Column

TABLE 1 Approximate Single Laboratory Detection Limits in Reagent Water[A,B]

Analyte	Peak No.	Retention Time, min	MDL mg/L
Fluoride	1	1.2	0.01
Chloride	2	1.7	0.02
Nitrite-N	3	2.0	0.004
Bromide	4	2.9	0.01
Nitrate-N	5	3.2	0.002
o-Phosphate	6	5.4	0.003
Sulfate	7	6.9	0.02

[A] Data provided by US EPA/EMSL Laboratory, Cincinnati, OH.
[B] Column: as specified in 7.1.4.
Detector: as specified in 7.1.6.
Eluent: as specified in 8.3.
Pump rate: 2.0 mL/min.
Sample loop: 50 µL.

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *analytical columns, n*—a combination of one or more guard columns followed by one or more separator columns used to separate the ions of interest.

3.2.1.1 *Discussion*—It should be remembered that all of the columns in series contribute to the overall capacity of the analytical column set.

3.2.2 *suppressor device, n*—a device that is placed between the analytical columns and the detector.

3.2.2.1 *Discussion*—The purpose of the suppressor is to minimize detector response of ionic constituents in the eluent, which lowers the detector background and at the same time enhances detector response to the ions of interest.

3.2.3 *eluent, n*—the ionic mobile phase used to transport the sample through the system.

3.2.4 *guard column, n*—a column used before the separator column to protect the analytical column from contaminants, such as particulate matter or irreversibly retained materials.

3.2.5 *ion chromatography, n*—a form of liquid chromatography in which ionic constituents are separated by ion exchange followed by a suitable detection.

3.2.6 *resolution, n*—the ability of an analytical column to separate constituents under specific test conditions.

3.2.7 *separator column, n*—the ion-exchange or analytical column used to separate the ions of interest according to the ion retention characteristics prior to their detection.

4. Summary of Test Method

4.1 An aliquot of sample is injected into an ion chromatograph. The sample is pumped through two columns, a suppressor device, and into a conductivity detector. The analytical column and the guard column are packed with anion exchange resin. Ions are separated based on their affinity for the exchange sites of the resin. The suppressor device contains a fiber- or membrane-based cation exchanger that is continuously regenerated by either a flow of dilute sulfuric acid or an electrolytic suppressor which does not require sulfuric acid. The suppressor device reduces the background conductivity of the eluent to a low or negligible level by replacing the cations with the hydrogen ion, thereby converting the anions in the sample to their corresponding acids. The separated anions in their acid form are measured using an electrical-conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

5. Significance and Use

5.1 Ion chromatography provides for both qualitative and quantitative determination of seven common anions, F^-, Cl^-, NO_2^-, HPO_4^{-2}, Br^-, NO_3^-, and SO_4^{-2}, in the milligram per liter range from a single analytical operation requiring only a few milliliters of sample and taking approximately 10 to 15 min for completion. Additional anions, such as carboxylic acids, can also be quantified.

NOTE 2—This test method may be used to determine fluoride if its peak is in the water dip by adding one mL of eluent (at 100× the concentration in 8.3) to all 100-mL volumes of samples and standards to negate the effect of the water dip. (See 6.3, and also see 6.4.) The quantitation of unretained peaks should be avoided. Anions such as low molecular weight organic acids (formate, acetate, propionate, etc.) that are conductive coelute with fluoride and would bias fluoride quantitation in some drinking waters and most wastewaters. The water dip can be further minimized if measures are taken to remove carbonic acid which remain in the eluent after suppression using carbonate based eluents. There is no water dip if hydroxide eluents are used.

5.2 Anion combinations such as Cl^-/Br^- and NO_2^-/NO_3^-, which may be difficult to distinguish by other analytical methods, are readily separated by ion chromatography.

6. Interferences

6.1 Since chloride and nitrite elute very close together, they are potential interferents for each other. It is advisable not to have one of these anions present in a ten-fold excess over the other; that is, Cl^-/NO_2^- ratios higher than 1:10 or 10:1 if both ions are to be quantitated or refer to newer column technology.

6.2 As with other types of chromatography, if one of the sample components is present at very high levels, it may interfere by causing a very large peak on the chromatogram that could mask other peaks present. This type of interference is normally minimized by dilution of the sample (see Annex

A1) and in some instances may be corrected if the concentration of that anion is of interest. However, care should be taken not to dilute the analyte concentration below its detectable limit.

6.3 Water from the sample injection will cause a negative peak or dip in the chromatogram when it elutes, because its conductivity is less than that of the suppressed eluent. This dip usually occurs before Cl^-. Any peak of interest eluting near the water dip must be sufficiently resolved from the dip to be accurately quantified. Some suggested techniques for elimination of the water dip are described in Appendix X1.

6.4 There may be a water dip and the interference of organic acids and due to the presence of carbonate ions in the separator column, the user of this test method is urged to use caution when determining fluoride (see Note 2). If the user wishes to be certain of good results and has interfering anions present when determining fluoride, the eluent can be diluted until separation of fluoride and carbonate is accomplished. This will cause an increase in retention time for anions such as sulfate to elute. Additional steps to avoid the water dip are mentioned in Appendix X1.

7. Apparatus

7.1 *Ion Chromatograph*—The ion chromatograph should have the following components assembled, as shown in Fig. 2:[4]

7.1.1 *Eluent and Regenerant Containers.*

7.1.2 *Eluent Pump,* capable of delivering 1 to 3 mL/min of eluent at a pressure of up to 2000 psi.

[4] Available from Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086. An equivalent may be used. Other manufacturers' components may provide equivalent data.

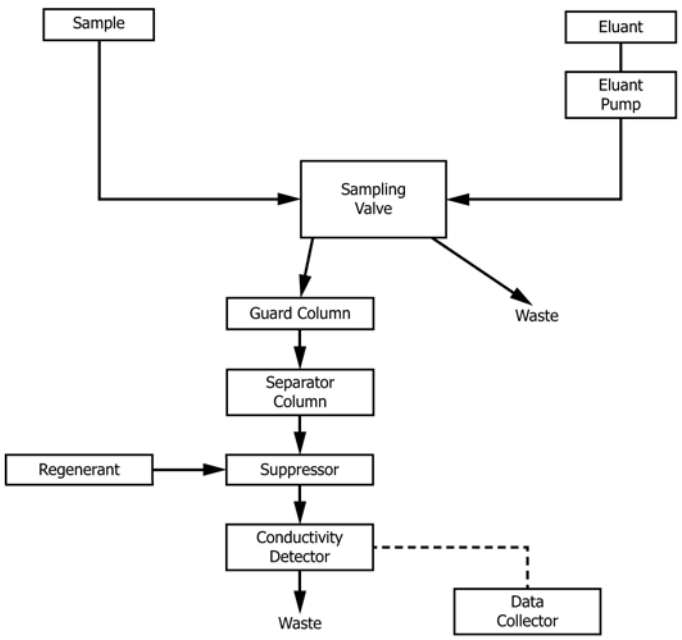

FIG. 2 Schematic of an Ion Chromatograph

7.1.3 *Guard Column*—Anion exchange column, typically of the same anion exchange material used in the separator column. The purpose of this column is to protect the analytical column from particulate matter and irreversibly retained materials.

7.1.4 *Analytical Column*—Anion exchange column capable of separating chloride from the injection void volume, as well as resolving the anions chloride through sulfate.

NOTE 3—Any analytical column may be used. However, the user should be able to achieve the resolution and separation as shown in Fig. 1.

7.1.5 *Suppressor Device*—A suppressor device based upon cation-exchange principles. In this method a membrane-based self-regenerating suppressor device was used. An equivalent suppressor device may be used provided that comparable method detection limits are achieved and that adequate baseline stability is attained. An electrolytic suppressor device can be used which does not require the addition of an acid but is a plug in electrolytic device. The suppressed eluent (water) is simply recirculated from the conductivity cell back to the electrolytic suppressor to back flush the suppressor device. Alternative pumps are also typically not required.

7.1.6 *Detector*—A low-volume, flow through, temperature-compensated electrical conductivity cell equipped with a meter capable of reading from 0 to 1000 µS/cm on a linear scale or greater if applicable.

7.1.7 *Recorder, Integrator, Computer*—A device compatible with the detector output capable of recording detector response as a function of time for the purpose of measuring peak height or area.

7.1.8 *Sample Loop*—A loop on the injection valve that is designed to contain an exact amount of the sample. The most common size is 100 µL. The sample volume injected onto the separator column is controlled by this loop. Use of a larger size loop will usually cause peak broadening and a loop size greater than 1 mL may result in column overloading and nonlinear response. The chromatogram in Fig. 1 uses a 100-µL size sample loop.

7.1.8.1 When injections of volumes larger than the sample loop size are made, any volume above the sample loop size goes to waste. It is considered good technique to flush the sample loop upon injection by injecting 2 to 3 times the sample loop volume.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

[5] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Analar Standards for Laboratory Chemicals," BDH Ltd., Poole, Dorset, U.K., and the "United States Pharmacopeia."

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type II; Type I may also be used. Column life may be extended by passing Type II water through a 0.22 µm filter prior to use. Freshly prepared water should be used for making the standards intended for calibration. The detection limits of this test method will be limited by the purity of the water and reagents used to make the standards. The purity of the water may be checked by use of this test method. Anion concentrations of less than 0.2 µg/L each are typical of this type of water.

8.3 *Eluent*—Dissolve 0.2856 g of sodium bicarbonate (1.7 m*M*) and 0.3816 g of sodium carbonate (1.8 m*M*) in water and dilute to 2 L with water. Other eluents may also prove to be acceptable, provided they give the proper resolution between the component peaks. This eluent will act as a growth media for algae. For this reason the eluent should not be kept for longer than one month.

8.3.1 *Hydroxide Eluent*—If NaOH is manually prepared us 50% (w/w) NaOH using degassed, deionized water (18.2 megaohm-cm) to a final volume of 1000 µL using a volumetric flask. Avoid the introduction of carbon dioxide from the air into the 50% NaOH or the distilled water being used to make the eluent. Do not shake the 50% NaOH or pipette the required aliquot from the top of the solution where sodium carbonate may have formed. Eight grams or 5.25 mL of 50% NaOH makes a 100 mM solution. A positive pressure of an inert gas should be maintained over the headspace to avoid carbon dioxide contamination. The used of electrolytically generated hydroxide by Reagent Free Ion Chromatography® to generate carbonate free hydroxide is also acceptable. In addition, electrolytically generated carbonate eluent is also acceptable. If using electrolytically prepared eluents only distilled water needs to be added to the system.

NOTE 4—Use of other eluents may change the order of elution of the anions from that using the carbonate-bicarbonate eluent.

8.4 *Fiber or Membrane Suppressor Regenerant Solution*—Cautiously add 3 mL of H_2SO_4 (sp gr 1.84) to 4 L of water. Not required for electrolytic or electronic based suppression.

8.5 *Stock Solutions:*

8.5.1 *Bromide Stock Solution* (1.00 mL = 1.00 mg Br^-)—Dry approximately 2 g of sodium bromide (NaBr) for 6 h at 150°C and cool in a desiccator. Dissolve 1.2877 g of the dried salt in water and dilute to 1 L with water. Alternatively, certified bromide stock solutions are commercially available through chemical supply vendors and may be used.

8.5.2 *Chloride Stock Solution* (1.00 mL = 1.00 mg Cl^-)—Dry sodium chloride (NaCl) for 1 h at 100°C and cool in a desiccator. Dissolve 1.648 g of the dry salt in water and dilute to 1 L with water. Alternatively, certified chloride stock solutions are commercially available through chemical supply vendors and may be used.

8.5.3 *Fluoride Stock Solution* (1.00 mL = 1.00 mg F^-)—Dissolve 2.210 g of sodium fluoride (NaF) in water and dilute to 1 L with water. Alternatively, certified fluoride stock solutions are commercially available through chemical supply vendors and may be used.

8.5.4 *Nitrate Stock Solution* (1.00 mL = 1.00 mg NO_3^-)—Dry approximately 2 g of sodium nitrate ($NaNO_3$) at 105°C for 48 h. Dissolve exactly 1.371 g of the dried salt in water and dilute to 1 L with water. Alternatively, certified nitrate stock solutions are commercially available through chemical supply vendors and may be used.

8.5.5 *Nitrite Stock Solution* (1.00 mL = 1.00 mg NO_2^-)—Place approximately 2 g of sodium nitrite ($NaNO_2$) in a 125-mL beaker and dry to constant weight (about 24 h) in a desiccator containing concentrated H_2SO_4. Dissolve 1.500 g of the dried salt in water and dilute to 1 L with water. Store in a sterilized glass bottle. Refrigerate and prepare monthly. Alternatively, certified nitrite stock solutions are commercially available through chemical supply vendors and may be used.

NOTE 5—Nitrite is easily oxidized, especially in the presence of moisture, and only fresh reagents are to be used.

NOTE 6—Prepare sterile bottles for storing nitrite solutions by heating for 1 h at 170°C in an air oven.

8.5.6 *Phosphate Stock Solution*(1.00 mL = 1.00 mg HPO^{4-2})—Dissolve 1.433 g of potassium dihydrogen phosphate (KH_2PO_4) in water and dilute to 1 L with water. Alternatively, certified phosphate stock solutions are commercially available through chemical supply vendors and may be used.

8.5.7 *Sulfate Stock Solution* (1.00 mL = 1.00 mg SO_4^{-2})—Dry sodium sulfate (Na_2SO_4) for 1 h at 105°C and cool in a desiccator. Dissolve 1.479 g of the dried salt in water and dilute to 1 L with water. Alternatively, certified sulfate stock solutions are commercially available through chemical supply vendors and may be used.

8.6 *Anion Working Solutions*—Prepare a blank and at least 3 different working standards containing the anions of interest. The combination anion solutions should be prepared in volumetric flasks. These standards must be prepared fresh daily. The concentration range for the three standards will be dependent on the levels expected in the samples. If desired, a single standard may be prepared that contains all six anions.

8.6.1 The user should select the ranges of the three standards so as to cover the entire range of the chart. The ranges chosen should all fall into one attenuation setting. If a second attenuation setting must be used, it must be calibrated using three standards and a blank. The standard concentrations given in Table 2 and Table 3 are for example purposes.

TABLE 2 Preparation of Standard Solutions for Instrument Calibration

Anion	High-Range Standard		Intermediate-Range Standard, mg/L	Low-Range Standard, mg/L
	Milliliters of Each Stock Solution (1.00 mL = 1.00 mg), Diluted to 1000 mL	Anion Concentration, mg/L		
Fluoride (F^-)	10	10	1.0	0.2
Chloride (Cl^-)	10	10	1.0	0.2
Nitrite (NO_2^-)	20	20	2.0	0.4
Phosphate (HPO^{4-2})	50	50	5.0	1.0
Bromide (Br^-)	10	10	1.0	0.2
Nitrate (NO_3^-)	30	30	3.0	0.6
Sulfate (SO_4^{-2})	100	100	10.0	2.0

TABLE 3 Preparation of Standard Solutions for Determination of Retention Times

Stock Solution (1 mL = 1.00 mg)	Volume of Stock Solution per liter of Water, mL	Anion Concentration, mg/L
Fluoride	4	4
Chloride	4	4
Nitrite	10	10
Phosphate	50	50
Bromide	10	10
Nitrate	30	30
Sulfate	50	50

9. Sampling

9.1 Collect the sample in accordance with Practices D1066 and D3370 as applicable.

9.2 Analyze the samples as soon as possible after collection. Preservation by refrigeration at 4°C is required for nitrite, nitrate, or phosphate.

9.3 Filter the samples containing particulates through a prewashed 0.22-µm filter prior to analysis to avoid fouling or clogging the resin of the columns.

10. Calibration

10.1 *Determination of Retention Times:*

10.1.1 The retention time for each anion is determined by injecting a standard solution containing only the anion of interest and noting the time required for a peak to appear on the chromatogram. Retention times vary with operating conditions and are influenced by the concentration of ion(s) present. Prepare separate standard solutions in accordance with Table 3 by pipetting the designated aliquots of stock solutions prepared in Section 8 (8.5.1 through 8.5.7) into separate 1-L volumetric flasks. Analyze each standard of interest as defined in Section 11. Note the time in minutes for each peak to appear on the chromatogram.

NOTE 7—Some operators have reported unusually large shifts in retention time for nitrate with changes in concentration. If this occurs, care must be taken to ensure integration of the correct peak when integration is used for calculation.

10.1.2 Concentrations other than those listed in Table 3 may be used if they better approximate concentrations expected in the samples. Those concentrations listed will give about midscale response with a 1-V recorder input and a conductivity meter full-scale setting of 10 µS/cm.

10.1.3 Retention times as well as elution order vary with the column used. See Fig. 1 for example elution orders using carbonate based eluent. If hydroxide eluents are used, the elution order of sulfate and phosphate are reversed.

10.2 Analyze the blank and each of the prepared calibration solutions described in 8.7 in accordance with the defined procedure (see Section 11).

NOTE 8—If the concentrations of the sample ions of interest are known or estimated, the concentration of standard solutions prepared for instrument calibration may be varied to better approximate or bracket the concentration range of interest. Anions of no interest may be omitted.

NOTE 9—The mid-range combination anion standard may be used to verify resolution of all seven anions.

NOTE 10—Each analytical curve should be established using only one scale setting. Changing the scale setting may result in a slight change in the slope of the analytical curve.

10.3 Prepare analytical curves for each anion of interest by plotting on linear graph paper peak height or peak area versus the nominal concentration of the anion standard solution. Additionally, a quadratic fit can also be used.

NOTE 11—Some operators have reported a shift in slope of the phosphate calibration curve at approximately 30 mg/L HPO_4^{-2}. If such a shift in slope is observed, additional standard solutions covering the entire range of concentration should be prepared and analyzed in order to accurately define the slope of the curve. If an integrator is being used, it may be necessary to manually calculate phosphate concentrations above 30 mg/L HPO_4^{-2} in order to obtain maximum accuracy.

11. Procedure

11.1 Set up the ion chromatograph according to the manufacturer's instructions.

11.1.1 The detector ranges are variable. Normal operating ranges are from 1 to 30 µS/cm full scale. The range setting required for analyses will depend on the concentration of anions in the sample and should be chosen accordingly.

11.2 Equilibrate the system by pumping eluent through the analytical column and suppressor device and the detector until a stable baseline is obtained (approximately 15 to 20 min) and approximately 10 to 15 µS background conductivity for carbonate based eluent. This equilibration normally can be accomplished while the samples and standards are being prepared. The background is lower when using hydroxide eluent because hydroxide is reduced to water in the suppressor. When using carbonate based eluents, it is possible to lower the background using an additional carbonate removal device.

11.3 Load 2 to 3 mL of sample into the sample entry port using a syringe. Inject the sample into the eluent stream and record the ion chromatogram (see Fig. 1).

NOTE 12—Most plastic disposable syringes, if used, come in packages labeled as "sterile," but this does not necessarily imply that they are free of anions; therefore, these syringes should be flushed with water and sample or standard before use to minimize contamination.

12. Calculation

12.1 Compare the peak heights or areas noted for the anion(s) in the samples to the calibration curves prepared in 10.3 to determine the anion concentration in milligrams per liter:

$$\text{Anion concentration, mg/L} = A \times F$$

where:

A = milligrams per liter read from appropriate calibration, and

F = dilution factor if sample was diluted prior to analyses.

13. Precision and Bias[6]

13.1 The collaborative test of this test method was performed in reagent water, drinking water, and a wastewater of

[6] Supporting data are available from ASTM Headquarters. Request RR:D19-1147.

TABLE 4 Determination of Bias for Fluoride

Water	Amount Added, mg/L	Amount Found, mg/L	S_t	S_o	Bias, %
Reagent	0.26	0.25	0.08	0.11	–3.8
	0.34	0.29	0.11		–14.7
	2.12	2.12	0.07	0.12	0.0
	2.55	2.48	0.14		–2.7
	6.79	6.76	0.20	0.19	–0.4
	8.49	8.46	0.30		–0.4
Drinking	0.26	0.24	0.08	0.05	–7.7
	0.34	0.34	0.11		0.0
	2.12	2.09	0.18	0.06	–1.4
	2.55	2.55	0.16		0.0
	6.79	6.84	0.54	0.25	+0.7
	8.49	8.37	0.75		–1.4
Waste	0.26	0.25	0.15	0.06	–3.8
	0.34	0.32	0.08		–5.9
	2.12	2.13	0.22	0.15	+0.5
	2.55	2.48	0.16		–2.7
	6.79	6.65	0.41	0.20	–2.1
	8.49	8.27	0.36		–2.6

choice by 19 laboratories using one operator each. Six levels of concentration were used for seven anions, producing three youden pairs. Each youden pair was used to calculate the single operator precision (S_o).

13.2 The precision and bias of this test method for each anion for reagent water, drinking water, and wastewater are shown in Tables 4-11.

13.3 Some of the bias statements, for example chlorine and sulfate, may be misleading due to spiking of small increments of the anion onto large naturally occurring concentrations of the same anion.

13.4 All data in Tables 4-10 were obtained using a non-metallic pump surface so as to minimize potential metallic contamination to the analytical columns.

13.5 This section on precision and bias conforms to Practice D2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D2777 – 08, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

TABLE 5 Determination of Bias for Chloride

Water	Amount Added, mg/L	Amount Found, mg/L	S_t	S_o	Bias, %
Reagent	0.78	0.79	0.17	0.29	+1.3
	1.04	1.12	0.46		+7.7
	6.50	6.31	0.27	0.14	–2.9
	7.80	7.76	0.39		–0.5
	20.8	20.7	0.54	0.62	–0.5
	26.0	25.9	0.58		–0.4
Drinking	0.78	0.54	0.35	0.20	–30.8
	1.04	0.51	0.38		–51.0
	6.50	5.24	1.35	1.48	–19.4
	7.80	6.02	1.90		–22.8
	20.8	20.0	2.26	1.14	–3.8
	26.0	24.0	2.65		–7.7
Waste	0.78	0.43	0.32	0.39	–44.9
	1.04	0.65	0.48		–37.5
	6.50	4.59	1.82	0.83	–29.4
	7.80	5.45	2.02		–30.1
	20.8	18.3	2.41	1.57	–11.8
	26.0	23.0	2.50		–11.5

TABLE 6 Determination of Bias for Nitrite–Nitrogen

Water	Amount Added, mg/L	Amount Found, mg/L	S_t	S_o	Bias, %
Reagent	0.36	0.37	0.04	0.04	+2.8
	0.48	0.48	0.06		0.0
	3.00	3.18	0.12	0.06	+6.0
	3.60	3.83	0.12		+6.4
	9.60	9.84	0.36	0.26	+2.5
	12.0	12.1	0.27		+0.6
Drinking	0.36	0.30	0.13	0.03	–16.7
	0.48	0.40	0.14		–16.7
	3.00	3.02	0.23	0.12	+0.7
	3.60	3.62	0.22		+0.6
	9.60	9.59	0.44	0.28	–0.1
	12.0	11.6	0.59		–3.1
Waste	0.36	0.34	0.06	0.04	–5.6
	0.48	0.46	0.07		–4.2
	3.00	3.18	0.13	0.10	+6.0
	3.60	3.76	0.18		+4.4
	9.60	9.74	0.49	0.26	+1.5
	12.0	12.0	0.56		+0.3

TABLE 7 Determination of Bias for Bromide

Water	Amount Added, mg/L	Amount Found, mg/L	S_t	S_o	Bias, %
Reagent	0.63	0.69	0.11	0.05	+ 9.5
	0.84	0.85	0.12		+ 1.2
	5.24	5.21	0.22	0.21	– 0.6
	6.29	6.17	0.35		–1.9
	16.8	17.1	0.70	0.36	+1.6
	21.0	21.3	0.93		+1.5
Drinking	0.63	0.63	0.13	0.04	0.0
	0.84	0.81	0.13		–3.6
	5.24	5.11	0.23	0.13	–2.5
	6.29	6.18	0.30		–1.7
	16.8	17.0	0.55	0.57	+0.9
	21.0	20.9	0.65		–0.4
Waste	0.63	0.63	0.15	0.09	0.0
	0.84	0.85	0.15		+1.2
	5.24	5.23	0.36	0.11	–0.2
	6.29	6.27	0.46		–0.3
	16.8	16.6	0.69	0.43	–1.0
	21.0	21.1	0.63		+0.3

14. Quality Control

14.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing anions in water.

14.2 *Calibration and Calibration Verification:*

14.2.1 Analyze at least three working standards containing concentrations of anions in water that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.

14.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration.

TABLE 8 Determination of Bias for Nitrate–Nitrogen

Water	Amount Added, mg/L	Amount Found, mg/L	S_t	S_o	Bias, %
Reagent	0.42	0.42	0.04	0.02	0.0
	0.56	0.56	0.06		0.0
	3.51	3.34	0.15	0.08	−4.8
	4.21	4.05	0.28		−3.8
	11.2	11.1	0.47	0.34	−1.1
	14.0	14.4	0.61		+2.6
Drinking	0.42	0.46	0.08	0.03	+9.5
	0.56	0.58	0.09		+3.6
	3.51	3.45	0.27	0.10	−1.7
	4.21	4.21	0.38		0.0
	11.2	11.5	0.50	0.48	+2.3
	14.0	14.2	0.70		+1.6
Waste	0.42	0.36	0.07	0.06	−14.6
	0.56	0.40	0.16		−28.6
	3.51	3.19	0.31	0.07	−9.1
	4.21	3.84	0.28		−8.8
	11.2	10.9	0.35	0.51	−3.0
	14.0	14.1	0.74		+0.4

TABLE 9 Determination of Bias for *ortho*-Phosphate

Water	Amount Added, mg/L	Amount Found, mg/L	S_t	S_o	Bias, %
Reagent	0.69	0.69	0.06	0.06	0.0
	0.92	0.98	0.15		+6.5
	5.77	5.72	0.36	0.18	−0.9
	6.92	6.78	0.42		−2.0
	18.4	18.8	1.04	0.63	+2.1
	23.1	23.2	0.35		+0.4
Drinking	0.69	0.70	0.17	0.17	+1.4
	0.92	0.96	0.20		+4.3
	5.77	5.43	0.52	0.40	−5.9
	6.92	6.29	0.72		−9.1
	18.4	18.0	0.68	0.59	−2.2
	23.1	22.6	1.07		−2.0
Waste	0.68	0.64	0.26	0.09	−7.2
	0.92	0.82	0.28		−10.9
	5.77	5.18	0.66	0.34	−10.2
	6.92	6.24	0.74		−9.8
	18.4	17.6	2.08	1.27	−4.1
	23.1	22.4	0.87		−3.0

TABLE 10 Determination of Bias for Sulfate

Water	Amount Added, mg/L	Amount Found, mg/L	S_t	S_o	Bias, %
Reagent	2.85	2.83	0.32	0.52	−0.7
	3.80	3.83	0.92		+0.8
	23.8	24.0	1.67	0.68	+0.8
	28.5	28.5	1.56		−0.1
	76.0	76.8	3.42	2.33	+1.1
	95.0	95.7	3.59		+0.7
Drinking	2.85	1.12	0.37	0.41	−60.7
	3.80	2.26	0.97		−40.3
	23.8	21.8	1.26	0.51	−8.4
	28.5	25.9	2.48		−9.1
	76.0	74.5	4.63	2.70	−2.0
	95.0	92.3	5.19		−2.8
Waste	2.85	1.89	0.37	0.24	−33.7
	3.80	2.10	1.25		−44.7
	23.8	20.3	3.19	0.58	−14.7
	28.5	24.5	3.24		−14.0
	76.0	71.4	5.65	3.39	−6.1
	95.0	90.3	6.80		−5.0

TABLE 11 Quality Control (QC) Sample Precision and Bias Data from Linear Regression Equations in mg/L

Water	Anion	True Value of QC's	Mean Rec. of QC's	S_t of QC's
Reagent	F^-	2.01	1.98	0.128
	Cl^-	10.00	9.94	0.490
	NO_2^-	5.00	5.18	0.170
	Br^-	5.00	5.02	0.265
	NO_3^-	5.01	4.93	0.256
	HPO_4^-	7.01	7.03	0.383
	SO_4^{-2}	25.00	25.17	1.58
Drinking	F^-	2.01	2.00	0.203
	Cl^-	10.00	8.55	1.88
	NO_2^-	5.00	4.97	0.295
	Br^-	5.00	4.95	0.240
	NO_3^-	5.01	5.03	0.336
	HPO_4^-	7.01	6.71	0.540
	SO_4^{-2}	25.00	23.07	2.02
Waste	F^-	2.01	1.97	0.170
	Cl^-	10.00	7.95	2.33
	NO_2^-	5.00	5.15	2.35
	Br^-	5.00	5.00	0.320
	NO_3^-	5.01	4.72	0.356
	HPO_4^-	7.01	6.53	0.746
	SO_4^{-2}	25.00	21.98	3.13

14.2.3 If calibration cannot be verified, recalibrate the instrument.

14.3 *Initial Demonstration of Laboratory Capability:*

14.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

14.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of anions in water. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

14.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Tables 4-11. This study should be repeated until the recoveries are within the limits given in Tables 4-11. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the *F* test and *t* test in evaluating the acceptability of the mean and standard deviation.

14.4 *Laboratory Control Sample (LCS):*

14.4.1 To ensure that the test method is in control, analyze a LCS containing a known concentration of anions in water with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples. The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within ±15 % of the known concentration.

14.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must

be qualified with an indication that they do not fall within the performance criteria of the test method.

14.5 *Method Blank:*

14.5.1 Analyze a reagent water test blank with each batch. The concentration of anions in water found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of anions in water is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.6 *Matrix Spike (MS):*

14.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of anions in water and taking it through the analytical method.

14.6.2 The spike concentration plus the background concentration of anions in water must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

14.6.3 Calculate the percent recovery of the spike (P) using the following formula:

$$P = 100[A(V_s + V) - B\,V_s]/C\,V \quad (1)$$

where:

A = analyte concentration (mg/L) in spiked sample,
B = analyte concentration (mg/L) in unspiked sample,
C = concentration (mg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

14.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Tables 4-11. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 13—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

14.7 *Duplicate:*

14.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

14.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

14.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.8 *Independent Reference Material (IRM):*

14.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

15. Keywords

15.1 anions; drinking water; ion chromatography; reagent water; wastewater

ANNEX

(Mandatory Information)

A1. DETERMINATION OF RANGE OF TEST METHOD

A1.1 The upper range of the test method for an injected aliquot varies for each sample type and is limited by the capacity of the separator column. If the ionic strength of the sample to be analyzed exceeds column capacity, the ions of interest will not be separated as shown in Fig. 1 and Fig. 2. Retention times will also decrease as the ionic strength of the sample increases. The upper range of the test method for the ion(s) of interest in the sample matrix may be determined by the following procedure. The procedure is defined for currently available separator columns supplied by the appropriate manufacturer.

A1.1.1 Bypass the separator column (only the suppressor is on-line) and inject 100 µL of 5.8 g/L (0.01 meq) solution of sodium chloride (NaCl). This represents 10 % of the separator column capacity, that is, 0.1 meq. Note the conductivity response.

A1.1.2 Inject 100 µL of the sample of interest (separator column bypassed). Note the conductivity response.

A1.1.3 If the conductivity response noted in A1.1.2 is less than or equal to the conductivity response noted in the sodium chloride solution in A1.1.1, column capacity has not been exceeded.

A1.1.4 If the conductivity response noted in A1.1.2 is greater than the conductivity response noted for the sodium chloride solution in A1.1.1, the test sample must be diluted prior to injection into the ion chromatograph.

APPENDIXES

(Nonmandatory Information)

X1. TECHNIQUES FOR ELIMINATING WATER DIP

X1.1 A method of eliminating the water dip is to introduce concentrations of carbonate and bicarbonate into the sample that closely approximate that of the eluent used for analysis. Adjustment of sample background may be accomplished in two different ways:

X1.1.1 Dilute the sample with eluent if sample dilution is required prior to analysis.

X1.1.2 Add an equivalent of 1.0 mL of a prepared eluent concentrate (solution that is 100 times more concentrated than the eluent used for analysis) per 100 mL of sample.

X1.2 Standard solutions must be prepared as directed in X1.1.2. It is important to prepare a blank using reagent water and eluent (100:1) to compensate for any anionic impurities present.

X1.3 Since this method was originally developed new column technology and instrument innovations have resulted in minimizing the water dip when using carbonate based eluents. For example, column development has allowed better resolution between the water dip and early eluting anions like Fluoride and organic acids. Refer to various manufacturers for further information.

X1.4 The use of hydroxide eluents does not result in a water dip since hydroxide is reduced to water in the suppressor.

X2. APPROVAL OF ELECTROLYTIC DEVICES AND REAGENT FREE ION CHROMATOGRAPHY (RFIC®)

X2.1 Since the development of this method and the original round robin data were first performed, new technologies have become available that have been shown to be reliable by many government laboratories for compliance monitoring for a wide variety of water matrices. The US EPA, ISO, ASTM, China SEPA, Japan Water Works are some examples of the regulatory agencies that have accepted the use of electrolytic devices for eluent generation, electrolytic suppression and electrolytic trap columns. The documents below are approval from the US EPA for electrolytic eluents. Based on this broad acceptance, ASTM recognizes the validity of these regulatory bodies and approves the use of electrolytic devices for eluent generation, regeneration, electrolytic suppression and electrolytic trap columns.

X2.2 The document below is the approval letter for the use of electrolytic eluent regeneration.

D 4327

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

NOV 1 9 2002

OFFICE OF
WATER

Douglas W. Later, Ph.D.
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Dear Dr. Later:

We are pleased to inform you that the Statistics and Analytical Support Branch (SASB) and the Office of Ground Water and Drinking Water's Technical Support Center (OGWDW/TSC) have determined that the use of hydroxide eluents (either manually prepared or electrolytically generated) falls within the method flexibility allowed in EPA Methods 300.0 and 300.1 for determining inorganic anions. Specifically, Sections 9.4.6 and 11.8 of Method 300.0 (Rev. 2.1, August 1993) and Section 9.4.5 of Method 300.1 (Rev. 1.0, 1997) state that the substitution of eluents to improve method performance is an acceptable method modification. Therefore, the use of hydroxide eluents in EPA Methods 300.0 and 300.1 is acceptable for compliance monitoring under the Clean Water Act and Safe Drinking Water Act. This determination supersedes all prior determinations on this subject and applies to all revisions of EPA Methods 300.0 and 300.1.

If you have any questions regarding this determination, please contact Khouane Ditthavong of SASB (202/566-1068) or Herb Brass of OGWDW/TSC (513/569-7936)

Sincerely,

William A. Telliard
Director of Analytical Methods
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for Herb Brass, Ph.D.
Technical Support Center (MS-140)
Office of Ground Water and Drinking Water

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8/15/2008

RE: ATP Case No. D07-0012

Per the terms of the Alternate Test Procedure (ATP) program, the Office of Ground Water and Drinking Water's Technical Support Center (OGWDW/TSC) has determined that the use of chromatographic systems that employ eluent regeneration are acceptable for use in EPA methods 300.0 and 300.1 when operated according to the manufacturer's instructions. Versions of these methods using eluent regeneration systems are determined to be acceptable versions of the original methods as long as all original method quality control parameters are met. Subsequently, these methods may be used for drinking water compliance monitoring performed under National Primary Drinking Water Regulations (NPDWR).

We appreciate your interest in the development of environmental monitoring methods. If you have any questions regarding the review of this alternate test procedure (ATP Case No. D07-0012), please contact Steve Wendelken by e-mail at: wendelken.steve@epa.gov or by telephone at: 513-569-7491.

Sincerely,

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SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D4327 – 03) that may impact the use of this standard.

(1) The scope was updated to include the use of electrolytic eluents and suppressors.
(2) 7.1.5 updated to include electrolytic suppression
(3) 8.3.1 updated to include the use of electrolytically generated eluents
(4) 8.5 was modified to allow for commercial standards.
(5) Section 11 updated discussion on water dip.
(6) 14.3.2 and 14.6.3 were modified.
(7) Updated Appendix to include reference to EPA approvals.